Kinetic Modeling of Cyclohexane Oxidation Including PAH Formation

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A reaction mechanism for cyclohexane (cyC_6H_{12}) is developed to study its oxidation at both low and high temperatures, including PAH formation. Based on values of rate coefficients available in literature, uncertainty analyses has been performed for each reaction class included in the mechanism, and the optimum values are implemented in the cyC_6H_{12} sub-mechanism. Furthermore, reactions of bi-cyclic ethers and cylohexanone decompositions via further dehydrogenation steps and ring-opening leading to smaller olefins and ketone radicals were implemented. Thermochemical properties of the main species of the low-temperature sub-mechanism are determined by applying the group additivity method of Benson. The properties of some new Benson's groups, including ring corrections for cycling species were estimated. The ignition delay data from rapid compression machines (RCM) and shock tube experiments and also laminar flame speed data have been used for the model validation. The concentration profiles of the soot precursor species from burner-stabilized premixed flames experiments at different pressures and temperatures are well predicted by the current model.

I. Introduction

CYCLOALKANES (naphthenes) are an important chemical class of hydrocarbons found in diesel (up to 35%), kerosene (~20%) and gasoline (~10%), which affects the ignition quality of the fuel. Also cycloalkanes can raise soot emission levels because they are known to dehydrogenate and produce aromatics which can initiate the chain reaction for the production of polycyclic aromatics to soot formation and growth. The combustion of cyclohexane (CHX, cyC_6H_{12}), the base simplest cycloalkanes, has been intensively investigated.[1-29] Table 1 summarizes the data-pool used in this study to develop the reaction mechanism. It shows the conditions of key experiments[11-20] as well as the experimental setup used to obtain these data. Despite these investigations on cyclohexane oxidation, the published primary reaction classes and their reference kinetic parameters show significant discrepancies. The uncertainty factor of reaction rate coefficients, $\Delta \log(k)$, for these reaction classes can reach almost 10.

The principal products of the cyclohexane pyrolysis were studied by Tsang in 1978[25] in shock tube experiments. Ethylene, 1,3-butadiene, and 1- hexene were identified as the main pyrolysis products. One of the first studies of low temperature chemistry of cyC_6H_{12} oxidation was performed by Zeelenberg and Bruijn[26] which analyzed the primary products of the slow oxidation of cyclohexane during the induction period at low temperature and low pressure. A further investigation of the low temperature oxidation with extensive analyses of various reaction paths was undertaken by Klaï and Baronnet.[27]

In the present work the high temperature scheme is developed further through extended cascading dehydrogenation steps and the low temperature chain propagation scheme includes formation of cyclohexanone and three bicyclic ethers and their decomposition paths. The required thermochemical properties specifically for low-temperature species, which have more complex structures, are revised and evaluated, applying Benson's additivity method with new available updates of Benson's groups[33] and ring corrections.

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Table 1. Kinetic mechanisms and their experimental validations[1-20] (ST = Shock tube, RCM = Rapid Compression Machine, PFR = Plug Flow Reactor, JSR = Jet Stirred Reactor).

Model	Validation				
	ST	**RCM**	**PFR**	**JSR**	**Flame Structure**
Voisin et al.[1]				**Concentration profile[13]** **T=** 750-1100 K, **τ** =0.5 s **P=** 10atm, **φ**=0.5, 1.0, 1.5 **Mixture (CHX/O_2):** (0.1,1.8),(0.1,0.9),(0.1,0.6)%	
El Bakali et al.[2]				**Concentration profile[1,13]** **T=** 750-1200 K, **τ** =0.07-0.5 s **P=** 1, 2, 10atm, **φ**=0.5, 1.0, 1.5 **Mixture (0.15%$CHX/O_2/N_2$)**	**Flame Speed[12]** **T=** 298 K **P=** 1atm
Ristori et al.[3]				**Concentration profile[3,13]** **T=** 980-1200 K **P=** 1atm, **φ**=1.0, **τ** =0.07 s **Mixture (Fu/ O_2/ N_2):** (0.15/1.35/98.5) %	
Granata et al.[4]		**Ignition delay time[11]** **P_{TDC}=** 0.7-0.9 Mpa **T=** 650-900 K **, φ**=1.0 Mixture (CHX/ air)	**Concentration profile[14]** **T=** 1155 K**, P=** 1atm **Mixture (MCH in N_2):** MCH= 0.166 vol.% **T=** 1160 K**, P=** 1atm **Mixture ($MCH/O_2/N_2$):** (0.185/1.9) vol.%	**Concentration profile**[1,2] **T=** 800-1200 K **,** **P=** 1-10atm **φ**=0.5, 1.0, 1.5	**Flame Speed[12]** **T=** 298 K **P=** 1atm
Dayma et al.[5]	**Ignition delay time[5]** **T=** 1050-1520 K**,** **P=** ~ 8atm **φ**=0.5, 1.0, 2.0				
Zhang et al.[6]					**Concentration profile[15,16]** **T=** 1000 K**,** **P=** 30 Torr **φ**=1.0, 2.0
Cavallotti et al.[7]		**Ignition delay time,** **Concentration profile**[11] **P_{TDC}=** 0.7-0.9/ 1.1-1.4 MPa **T=** 700-1000 K, **φ**=1.0 **Mixture:** CHX/ air		**Concentration profile[2]** **T=** 800-1200 K **P=** 1-10atm **φ**=0.5, 1.0, 1.5	
Silke et al.[8]		**Ignition delay time**[11] **P_{TDC}=** 0.7-0.9/1.1-1.4 MPa **T=** 700-1000 K, **φ**=1.0 **Mixture :**CHX/ air		**Concentration profile**[1] **T=** 850-1070 K**, P=** 10atm **φ** = 0.5, 1.0, 1.5, **τ** =0.5 s **[13]: (T/ P/ φ/ τ)** (850-1150 K/2 atm/1.0/0.1 s) (850-1150 K/5 atm/1.0/0.25 s) **Mixture:** CHX/ O_2 in 99% N_2	
Buda et al.[9]		**Ignition delay time[11]** **P=** 0.7-0.9/ 1.1-1.4 MPa **T=** 700-1000 K, **φ**=1.0 **Mixture :** CHX/ air		**Concentration profile**[1] **T=** 850-1070 K**, P=** 10atm **φ** = 0.5, 1.0, 1.5 , **τ** =0.5 s	
Serinyel et al.[10]	**Ignition delay time[19]** **T=** 950-1200 K **P=** 13-15 bar **φ**=0.5, 1.0	**Ignition delay time[11]** **P_{TDC}=** 1.1-1.4 Mpa **T=** 700-1000 K, **φ**=1.0 **Mixture:** CHX/ air **[20]:** **T=** 600-900 K, **φ** = 0.5,1.0,2 **P=** 12.5, 20, 40 bar **Mixture:** CHX/ O_2 in N_2 **X_{fuel}**=0.0226		**Concentration profile[10]** **T=** 500-1100 K **P=** 1.07 bar , **φ** = 0.5,1.0,2 **τ** = 2 s	**Flame Speed (Flat- flame)[10]** **T=** 298,358, 398 K **P=** 1atm **[12] (Counter flow):** **T=** 298 K - **P=** 1atm **[17] (Counter flow):** **T=** 353 K - **P=** 1atm **[18](spherical flame):** **T=** 353 K, **P=** 1-20 atm

II. Kinetic Model

The reaction mechanism has been developed for high and low temperature oxidation of cyclohexane using the base model of DLR (C_0-C_4 kinetic model[31] combined with a PAH formation sub-model[31,32]). During the cyclohexane mechanism development, the generic reactions for both regimes (high and low temperature) of the cyclo-hydrocarbon oxidation are determined. The cyclohexane high temperature oxidation (Fig.1) proceeds through:

1) unimolecular fuel decomposition
2) H-atom abstraction leading to cycloalkyl radical, cyC_6H_{11}
3) cyC_6H_{11} β-scission decomposition, producing olefins and di-olefins
4) cascading dehydrogenation leading to benzene and smaller radicals
5) isomerization and decomposition of linear hexenyl radicals after the ring-opening step.

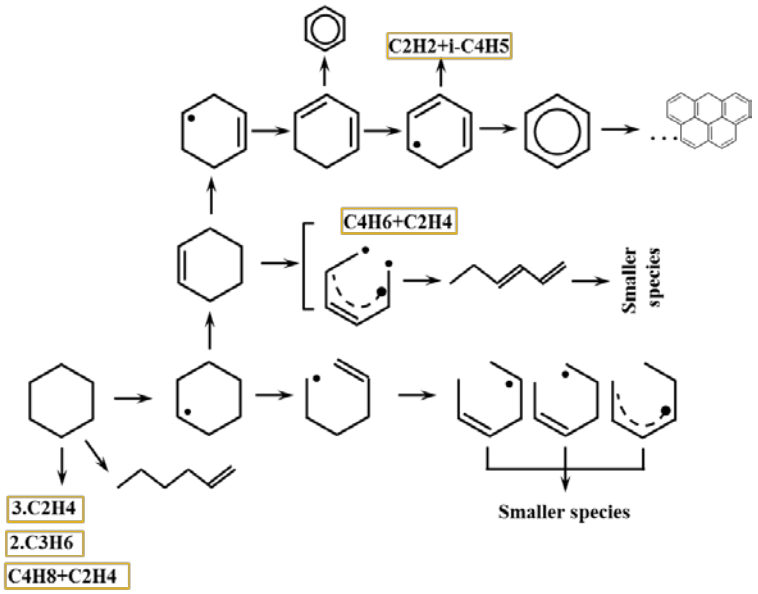


Figure 1. Principal scheme of the high temperature oxidation of cyC_6H_{12}.

The low temperature cyclohexane oxidation can be described with the general scheme for the low temperature oxidation of acyclic alkanes, but with the formation of intermediate species with 2 rings, specifically bi-cyclic ethers and cyclic ketones (Fig.2). The low temperature oxidation proceeds through :

1) $cyC_6H_{11}O•$ and cycloperoxy radical ($cyC_6H_{11}OO•$) formation from reactions of $cyC_6H_{11}•$ with O_2 and O•, leading to further chain branching pathways;
2) isomerization of $cyC_6H_{11}OO•$ to cyclohydroperoxy radicals ($cyC_6H_{10}OOH•$) through the 4-, 5-, 6-, and 7-centre transition states;
3) decomposition $cyC_6H_{11}OO•$ radicals to cyclohexene and HO_2 ;
4) Formation of $cyC_6H_{11}O•$ from $cyC_6H_{11}OO•$ radicals;
5) decomposition of $cyC_6H_{10}OOH•$ and $cyC_6H_{11}OO•$ radicals to cyclohexanone, three bicyclic ethers and smaller species;
6) O_2 addition to $cyC_6H_{10}OOH•$ with formation of $O_2QOOH•$ type radicals;
7) decomposition of bicyclic ethers and cyclohexanone through dehydrogenation leading to formation of cyC_6H_9O radicals.
8) decomposition of $O_2QOOH•$ to cyclic ketohydroperoxides;
9) HO_2 addition to cyC_6H_9O and formation of $cyOC_6H_9OO•$ ketohydroperoxides;
10) decomposition of cyclic ketohydroperoxides OQOOH to hydroxyl radical and smaller species;
11) decomposition of $cyC_6H_9O•$ via ring opening to small olefin molecules and ketone radicals.

The actual uncertainty levels of the main reaction rate coefficients have been analyzed, based on the data collected from literature. On these grounds the optimum values for each reaction have been evaluated and applied in the mechanism.

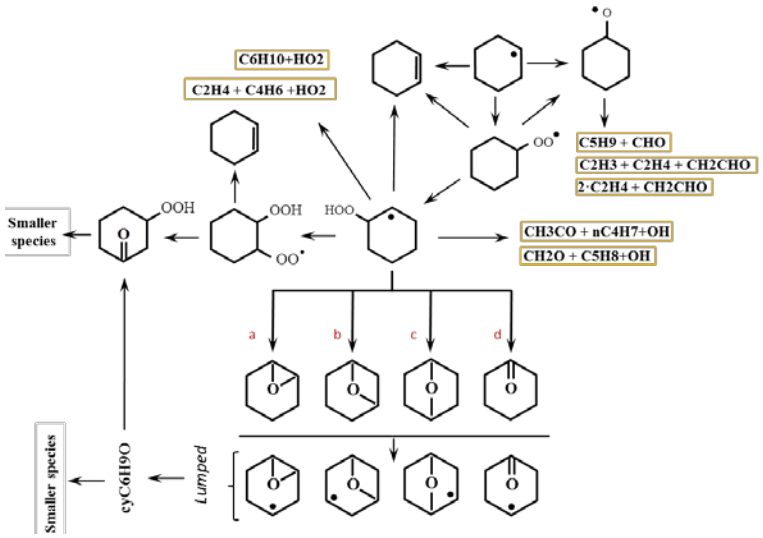


Figure 2. Principal scheme of the low temperature oxidation of cyC_6H_{12}.

The statistical treatment of the rate coefficient goes through certain number of available data is based on the least-squares regression. We used the non-linear least squares method and its numeric realization FUMILI.[40] This linearizes model and approximates the data of "*m*" observations with a model of "*n*" unknown parameters *(m > n)*. The evaluation of parameters is obtained, minimizing an objective function. An in house developed tool, written by DLR (German Aerospace Center) at Stuttgart was used for this aim. Fig.3 shows an example of uncertainty estimation and analysis for one of the reactions of high temperature regime, abstracting a hydrogen atom from cyclohexane molecules by O atom, initiating cyclohexane radicals. Table 2 represents the applied reaction rates and calculated uncertainty factors for lower (F_l) and upper (F_u) boundaries. Statistical uncertainty analysis is limited to the number of available data sets (observation). Therefore this was not performed for certain reactions, due to the lack of data.

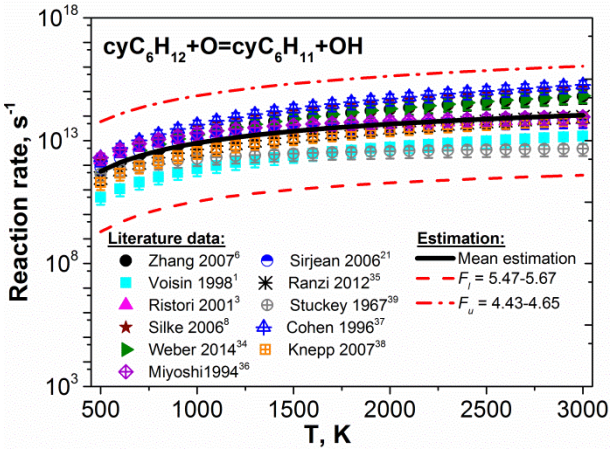


Figure 3. Uncertainty estimation and analysis of reaction rate vs. temperature, based on the available literature data for the reaction $cyC_6H_{12}+O=cyC_6H_{11}+OH$.

Estimation of the thermodynamic properties for certain species, including new species, was done based on the Benson's additivity method, with the updates and corrections especially for cyclic and bicyclic structures, reported in previous work of the authors.[33] Approximation of the NASA-polynomial function was also done, utilizing an in-house developed FORTRAN code, written by DLR (German Aerospace Center) at Stuttgart. The transportation properties were also extended using group contribution method of.[43]

Table 2. Reaction rate and estimated lower and upper uncertainty factors for major reaction types in high and low temperature regimes.

Reaction*	Type	ΔT, K	A	β	E_a	Ref.	F_l	F_u
High temperature								
$cyC_6H_{12} = cyC_6H_{11} + H$	DE-INT	500-3000	3.00E+16	0.0	95000	[3]	-**	-
$cyC_6H_{12} => 3C_2H_4$	DE	500-3000	8.22E+17	0.0	87225	[1]	2.33-3.78	0.92-2.37
$cyC_6H_{12} = aC_6H_{12}$	RN	1000-3000	5.01E+16	0.0	88230	[25]	5.88-6.20	4.85-5.17
$cyC_6H_{12}+O_2 = cyC_6H_{11} + HO_2$	HABS-INT	1000-3000	6.00E+12	0.0	50150.1	[6]	2.47-2.65	2.44-2.62
$cyC_6H_{12}+CH_3 = cyC_6H_{11} + CH_4$	HABS-INT	500-3000	1.35E+12	0.0	9540	[1]	2.38-2.64	2.35-2.61
$cyC_6H_{12}+C_2H_3 = cyC_6H_{11} + C_2H_4$	HABS-INT	500-3000	1.35E+12	0.0	9540	[1]	2.72-2.85	2.63-2.76
$cyC_6H_{11} = C_6H_{11}$	RN	1000-3000	3.00E+12	0.624	30810	[28]	2.82-2.92	2.71-2.80
$cyC_6H_{11} = cyC_6H_{10} + H$	BSC	1000-3000	8.91E+11	0.834	36340	[28]	3.38-3.57	3.07-3.26
$cyC_6H_{11}+O = C_5H_9 + CH_2O$	DE	500-3000	9.61E+13	0.0	0.0	[41]	-	-
$cyC_6H_{11}+O_2 = cyC_6H_{10} + HO_2$	HABS	700-3000	1.50E+12	0.0	4251.2	[6]	2.40-2.62	2.38-2.60
$cyC_6H_{11}+HO_2 = cyC_6H_{10} + H_2O_2$	HABS	600-3000	1.00E+12	0.0	2000	[1]	1.31-1.72	1.29-1.70
$cyC_6H_{11}+CH_3 = cyC_6H_{10} + CH_4$	HABS	500-3000	1.71E+13	0.0	0.0	*generic*	1.64-1.88	1.35-1.59
$cyC_6H_{10} = cyC_6H_9 + H$	DE	1200-3000	1.20E+15	0.0	83200	[5]	3.11-3.21	2.82-2.92
$cyC_6H_{10} = C_4H_6+C_2H_4$	DE	1200-3000	4.00E+14	0.0	63400	*generic*	1.46-1.71	1.17-1.42
Low Temperature								
$cyC_6H_{11}+O_2 = cyC_6H_{11}OO$	ADD	700-3000	8.00E+18	-2.5	0.0	[9]**a**	6.40-6.83	6.1-6.58
$cyC_6H_{11}OO = cyC_6H_{10}OOH$	ISM	800-3000	1.50E+12	0.0	24076	[43]**b**	5.58-6.33	5.53-6.29
$cyC_6H_{10}OOH => CH_2O + C_5H_8 + OH$	BSC	900-3000	2.20E+16	0.0	22500	[42]**c**	4.28-4.73	3.33-3.78
$cyC_6H_{10}OOH = a\text{-}cyC_6H_{10}O + OH$	DE2BCYE	500-3000	2.20E+16	0.0	22500	[7]	3.00-3.14	2.84-2.99
$cyOOC_6H_{10}OOH = OH + cyOC_6H_9OOH$	DE2CKHP	1000-3000	1.50E+16	0.0	42500	[42]**c**	2.87-2.92	2.77-2.82
$cyC_6H_{11}O => CH_2CHO + 2C_2H_4$	DE	500-3000	2.00E+13	0.0	25700	[5]	9.6-10.1	9.32-9.84

Notes:
***** Reaction rate constants in cm^3, *mol*, *cal* units, $k = AT^{\beta}exp(E/RT)$ ****** No analysis done, due to limited of sources.
a) The pre-exponent factor, *A* ,multiplied by 1.33 **b)** Analogous with C_8, *A* multiplied by 3.7, E_a added by 3.2 *kcal* **c)** Analogous with C_8

Abbreviations:
DE: Decomposition **INT**: Initiation **HABS**: H atom Abstraction **RN**: Ring-opening **BSC**: β- Scission **ADD**: Addition **ISM**: Isomerization **DE2BCYE**: Decomposition to bi-cyclic ethers **DE2CKHP**: Decomposition to cyclic Ketohydroperoxide

III. Results and discussion

The behaviour of the high and low temperature cyclohexane oxidation model was validated and optimized based on a) the simulation of ignition delay times over the temperature range of 650-1700K at various equivalence ratios and pressure ranges, b) Experimental data from Rapid Compression Machines (RCM)[11,20] and shock tubes (ST)[21] and c) laminar flame speed data[12] at standard room pressure and temperature. PAH formation was observed in laminar premixed cyclohexane flames,[6,16,22] see Table2 for details. The full sets of simulated data will be extensively presented in the full version of this work. In the following we present data in order to investigate the behaviour of the reaction model in high and low temperature range, at different pressures and at different compositions.

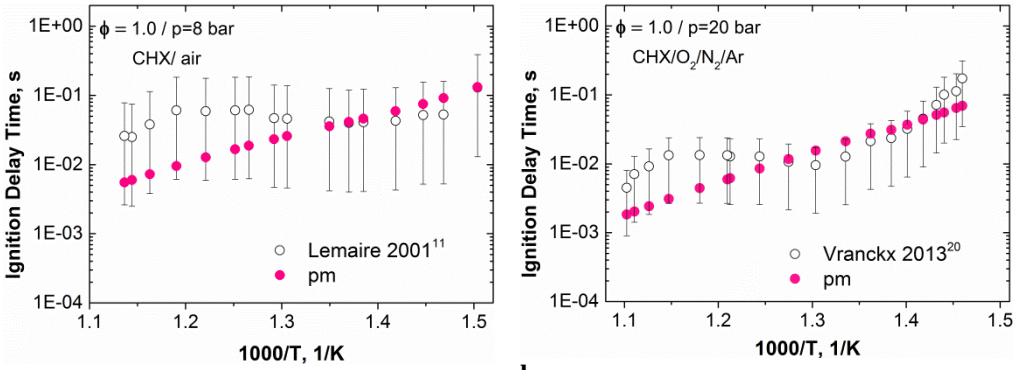
Table 3. Experimental data, used for validations.

Exp.	Validation		
	ST	**RCM**	**Flame Structure**
Law et al.[16]			**Concentration profile[15,16]** **T=** 1000 K, **P=** 30 Torr, **φ**=1.0 **Mixture:** CHX/O_2 in 32.5% Ar **MFR**=0.00214 $g.cm^{-2}.s^{-1}$
Vranckx et al.[20]		**Ignition delay time[20]** **T=** 600-900 K **φ** = 1.0, **P=** 12.5, 20 bar **Mixture:** CHX/air $\mathbf{X_{fuel}}$=0.0226	
Lemaire et al.[11]		**Ignition delay time** **P**= 8, 14 bar **T=** 650-900 K , **φ**=1.0 Mixture (CHX/ air)	

Sirjean et al.[21]	**Ignition delay time** **T=** 1230-1840 K, **P=** ~ 8atm **φ=**0.5, 1.0, 2.0 **Mixture:** CHX/O_2 in 90.5-97.25% Ar	
Ciajolo et al.[22]		**Concentration profile** **T=** 700 K, **P=** 1 atm, **φ=**2.33 **Mixture:** CHX/O_2 in 39.4% N_2 **MFR**=0.00283 $g.cm^{-2}.s^{-1}$
Richter et al.[23]		**Flame Speed** **T=** 473 K **P=** 0.1,0.3,0.6 MPa Mixture (fuel-O2-N2)
Nauman et al.[24]	**Ignition delay time** **T=** 800-1400 K, **P=** ~ 16atm **φ=**1.0 **Mixture:** CHX/O2/ 89% N2	

A. Ignition-delay-time

The simulation of experimental data for ignition delay times of[11] and[20]from Rapid Compression Machine (RCM) in the temperature range 650-900 K at 8 atm and 20 atm pressure are shown in Fig4. The measured data are reproduced successfully and under predicted uncertainty for the experimental data. However the negative temperature effects and the uprising of ignition delay time around 770-780 K, observed in both sets around, was not predicted by the model. With increase of temperature the direction of $cyC_6H_{11}+O_2 = cyC_6H_{11}OO$ changes and the equilibrium will be shifted to the left side, which leads to the negative temperature behaviour. As a result, production of cycloalkyl radicals increases and consequently the level of olefins raises. Due to the implemented values for reaction rate constants in this sub-mechanism and thermodynamic properties provided by this model, existence of any turning point in the direction of the mentioned equilibrium in 700-800K is not foreseen. Our further investigation shows that implementation of other suggested rate coefficients in literature in our sub-model, does not show any improvement in this case. Which other reaction paths are playing the key roles and could be applied in the model, would be one of the aims of our future cyclohexane kinetic research.



a **b**

Figure 4. Cyclohexane ignition delay time from RCM experiments: a) Lemaire et al.[11] for φ=1, p=8 bar and b) Vranckx, et al. (Aachen)[20] at φ=1.0 , p=20 bar. Closed colored symbols: Simulations, open symbols: experimental data with their uncertainties.

The experimental data from shock tube (ST) experiments under various circumstances and in different mixtures were also used for validation. Fig.5 shows the simulation versus experimental data for ignition delay times of[19],[21] and[24]. The ignition delay data from shock tube experiments (depending on the conditions) have normally lower level of uncertainties compared to RCM experiments. The results are in a satisfactory agreement with experimental points both in high and normal pressure, and in different mixture fractions (φ=0.5,1.0,2.0). Deviation of the predicted values are mainly less than the uncertainty considered for experiments. In contrary to low temperature results from RCM experiments, none of the studied ST experiments do not show the negative temperature behaviour and

simulation results especially for low temperatures match perfectly with experiments. However, as Fig.5c shows the ignition delay time for temperature range of 1160-1260 K in lean condition φ=0.5 and pressure of 12 bar, were not well reproduced by the model and the values are slightly over predicted.

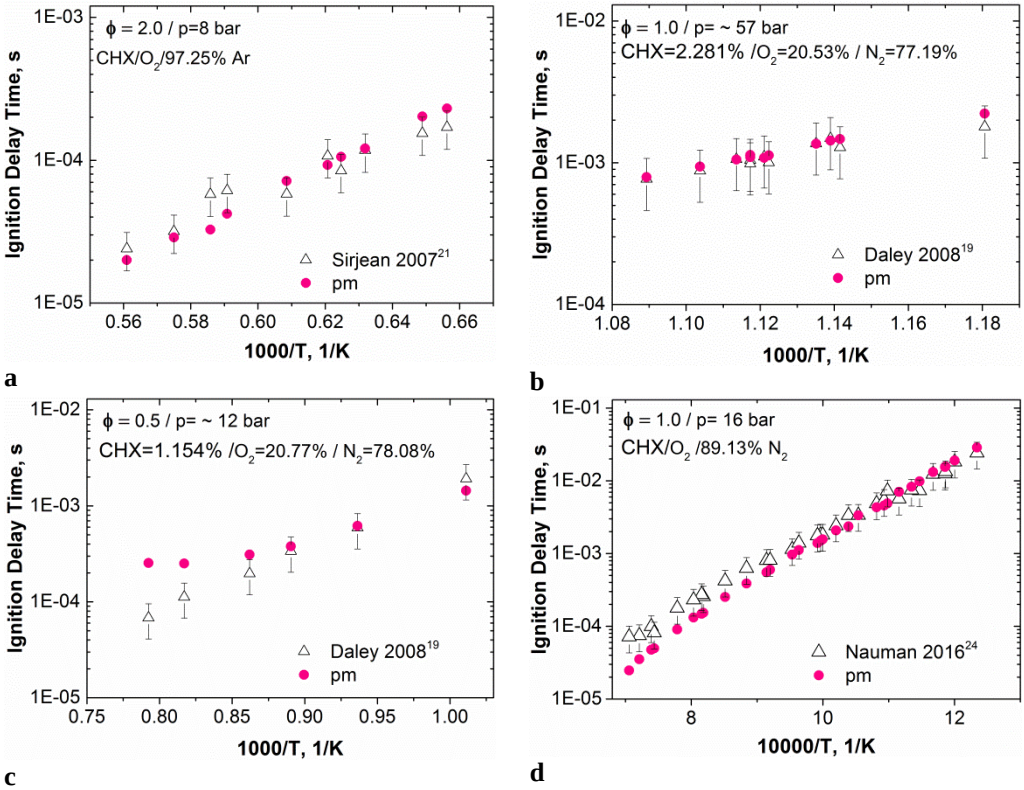


Figure 5. Cyclohexane ignition delay time from ST experiments: a) Sirjean et al.[21] in φ=2, p=8 bar diluted in Ar; ST experiments from Daley et al.[19], with N_2 dilution, in b) stoichiometric situation, p=57 bar c) φ=0.5 and p=12 bar; d)Nauman et al.[24] in φ=1.0 and p=16 bar. Closed colored symbols: Simulations, open symbols: experimental data with their uncertainties.

B. Laminar-flame-velocity

The flame speed values reported in[23] at p=1 atm and in elevated temperature of 473K were also used for validation. The results are presented in Fig.6.

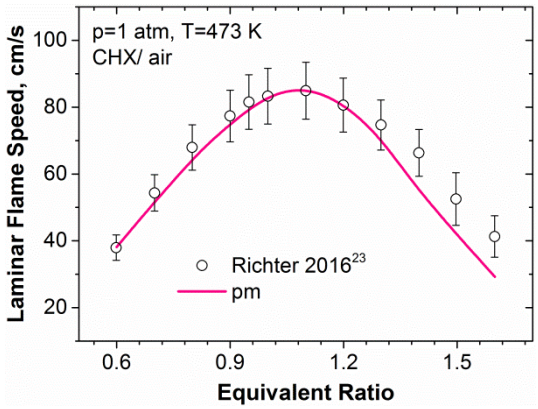


Figure 6. Cyclohexane laminar flame speed. The solid line-simulation; symbols- experimental data[23].

As it can be seen for φ=0.5-1.3 the simulation shows a perfect consistency with experimental data; as the ratio of fuel to oxidizer grows, the predicted values deviate slightly from experiment, however this should be taken into the account that the level of uncertainty of experiment grows, as the mixture goes richer.

C. Concentration profiles

Results of modeling the mole fraction profiles of some of the important PAH precursors, C_3H_6, cyC_5H_5, cyC_5H_6, cyC_6H_9 and C_6H_6 (Or A1, benzene)[6,16] at p=30 Torr and φ=1.0 are shown in Fig.7a-k. Simulated and experimental values are in a proper consistency with each other. Concentrations of cyC_5H_5 and C_3H_6 are over- predicted (see Fig.7g-h). Meanwhile, the concentration of C_6H_6 is by order of 10 is under estimated (Fig.7j). Also concentration of cyC_6H_9, predicted by the model is one order of magnitude above the observed values (Fig.7k). This means the model does not predict the sooting as high as observed by[16], which sounds reasonable due to the low pressure of 30 Torr, stoichiometric condition of the premix flame, uncertainty of the temperature and location measurements.

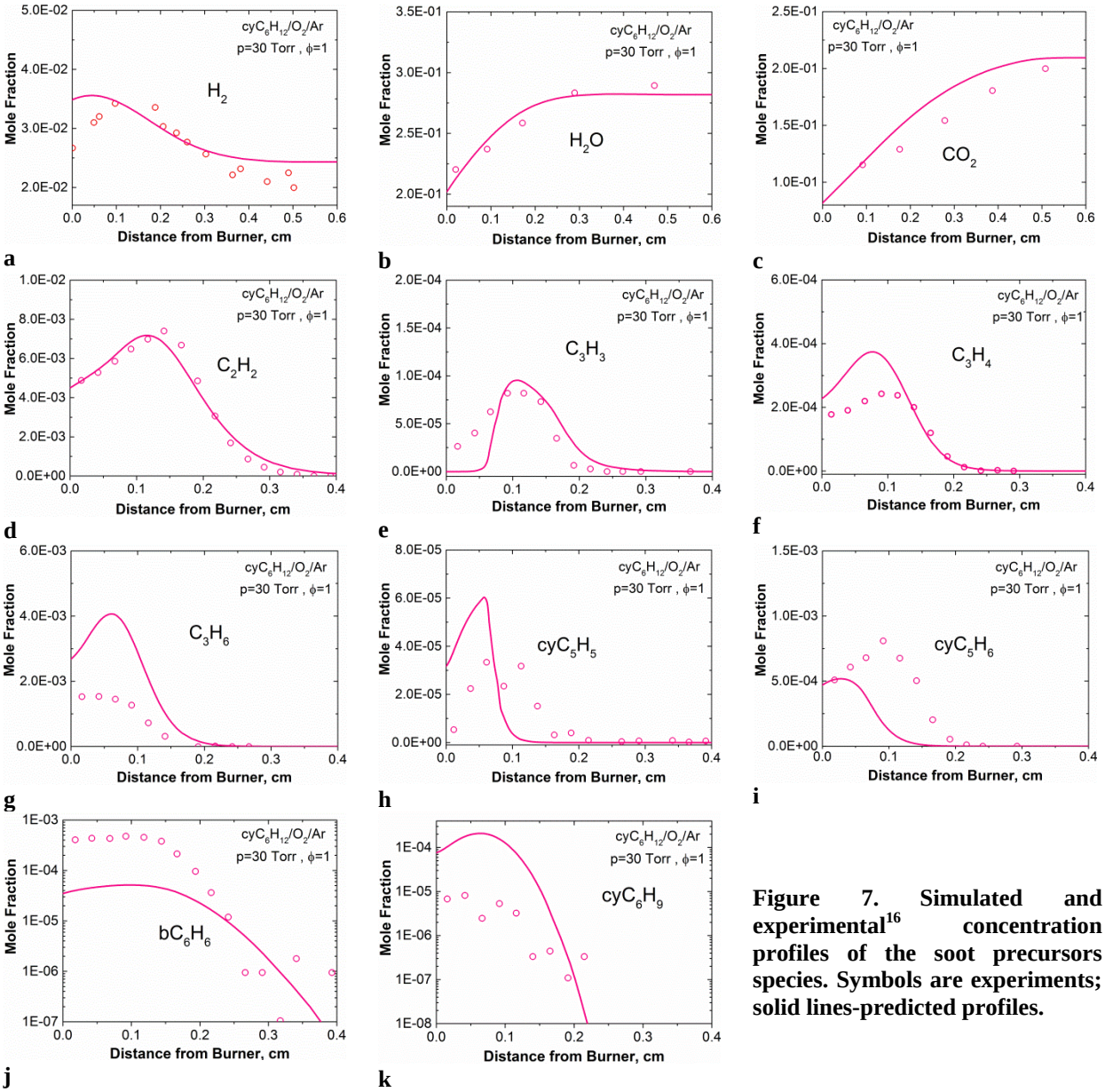


Figure 7. Simulated and experimental[16] concentration profiles of the soot precursors species. Symbols are experiments; solid lines-predicted profiles.

The fuel-rich premixed flame (φ=2.33) of [22] was also simulated in atmospheric pressure and the concentration of the major species were compared with reported profiles. Fig.8a-i show these comparisons. The concentration

profiles for reactants (cyC_6H_{12}, O_2), major products (CO, CO_2, H_2, CH_4 and C_2H_2) (see Fig.8a-d) and also for certain intermediates such as C_2H_2, C_4H_6 and C_3H_4 are excellently reproduced by the model. However, mole fractions of C_3H_6 and cyC_5H_6 are by factors around 3 and 10 respectively are over predicted. Unlikely to the previous data set of [16], where the mole fraction of C_6H_6 was considerably under estimated, here the concentration of benzene is described around 10 times higher than observed in[22]. Fig.8i shows the concentration profiles for C_4H_2 and C_4H_4. The former is simulated higher than measured values by a factor 10 and the latter is significantly under experimental data. Investigating on the reasons for these mismatches could be a part of the further researches.

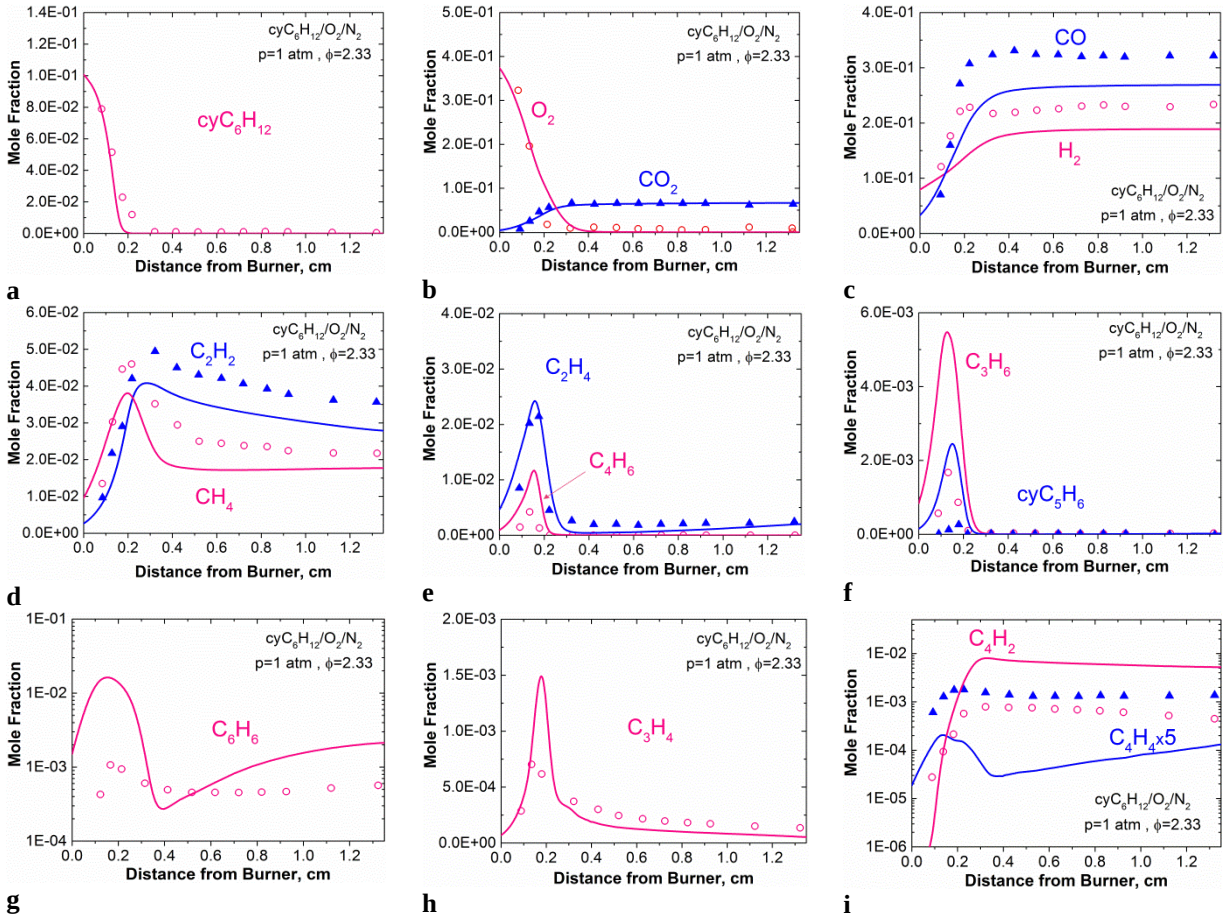


Figure 8. Simulated and experimental[22]concentration profiles of the soot precursors species. Symbols are experiments; solid lines-predicted profiles.

IV. Conclusions

A skeletal reaction mechanism for low and high temperature cyclohexane oxidation with PAH formation is reported. This mechanism is an extension of the DLR hydrocarbon reaction database by including the cycloalkane oxidation sub-model. The development of the mechanism was based on the data consistency and uncertainty analysis among the available literature data. The reaction model was successfully validated against experimental data for ignition delay times measured in rapid compression machines and shock tube experiments. Also, laminar flame specifications at low and atmospheric pressure and in stoichiometric and fuel-rich conditions were successfully validated. The important features of this mechanism are the new extended paths for both high and low temperature sub-mechanisms and its ability to predict the auto-ignition behavior in different conditions, as well as the laminar flame properties. The chemical pathways leading to intermediates and formation of PAH are well understood.

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